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<b>(21) International Application Number:</b> PCT/GB98/01872 <b>(22) International Filing Date:</b> 14 July 1998 (14.07.98)  <b>(30) Priority Data:</b> 9714905.8 16 July 1997 (16.07.97) GB  <b>(71) Applicants (for all designated States except US):</b> JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE [CH/CH]; CM-Ecublens, CH-1015 Lausanne (CH).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MURRER, Barry, Anthony [GB/GB]; 17 Carnarvon Road, Reading RG1 5SB (GB). GRAETZEL, Michael [DE/CH]; Chemin du Marquisat 7A, CH-1025 Saint Sulpice (CH). NAZEERUD-DIN, Mohammad, Khaja [IN/CH]; Chemin de la Chiesaz 9, CH-1024 Ecublens (CH).  <b>(74) Agent:</b> WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PHOTSENSITIZERS		
<b>(57) Abstract</b>  Novel transition metal phthalocyanine-type compounds having an axial ligand which is capable of binding onto a semiconductor such as TiO <sub>2</sub> , and having at least one peripheral substituent, are active photosensitizers for dye solar cells. Preferred compounds offer absorbance of solar radiation in the near infra-red and may be used in electricity-generating windows.		

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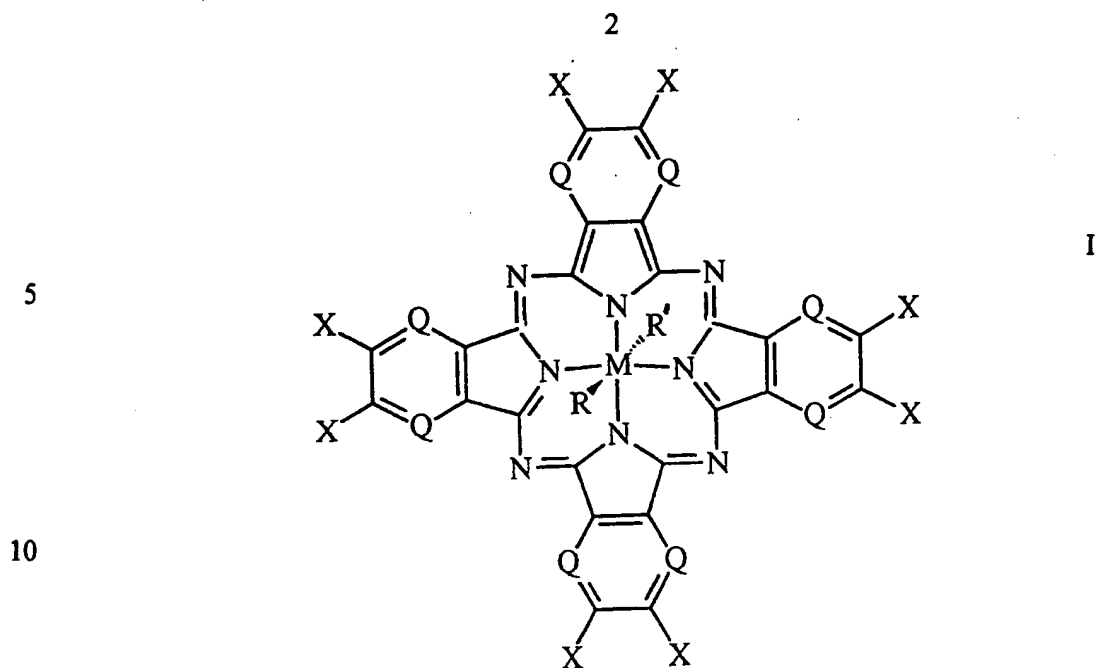
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## PHOTOSENSITIZERS

This invention concerns photosensitizers, more particularly it concerns novel  
5 transition metal photosensitizers.

Various metallated phthalocyanine derivatives have been suggested as potential  
photodynamic therapy agents, *ie* as photosensitizers in the treatment of tumours, see for  
example Rosenthal, Photochem Photobiol, 53 (6), 859-870 (1991) and our published  
10 International Application WO 93/09124. An interesting new photosensitizing field, is the  
use of optical brighteners and phthalocyanines as photosensitizers in photovoltaic cells (see  
WO 91/16719 (Graetzel) and WO 94/05025 (Sandoz)) based on  $\text{TiO}_2$ . We understand that  
a number of companies are developing photovoltaic cells based on this technology. The  
currently recommended dye-type sensitizer is cis-di(thiocyanato)bis(2,2'-bipyridine-4,4'-  
15 dicarboxylate) ruthenium(II), (I) known as "RuN3 dye". RuN3 dye has an excellent photon  
to electron conversion, and very high stability. Certain metallated phthalocyanines have  
been tested, but their electrical output is not nearly as high as the RuN3 dye. Despite the  
high efficiency and output of photovoltaic devices based on the RuN3 dye, and their  
particularly useful property of continuing to have high output under cloudy conditions  
20 (unlike silicon-based photocells), they do have a purple colour. There remains the need for  
alternative photosensitizers for use with  $\text{TiO}_2$ -based photovoltaic devices, especially those  
which absorb at longer wavelengths than RuN3. Such sensitizers may absorb in the near  
infra-red region and may possibly be used to make optically transparent photovoltaic devices  
useful for example in windows or other glazed areas. When combined with a conventional,  
25 visible spectrum, photosensitizer such as RuN3, then solar energy from a wider spectrum  
may be converted to electricity, giving an increased efficiency for the device.

The present invention provides novel transition metal phthalocyanine-type  
derivatives of formula I,



wherein M is Ru, Rh, Os, Ir or Pt

15 each X is hydrogen, alkyl, alkoxy, hydroxy, aryl, substituted aryl, alkylthio, ether, thioether, amino or mono- or di-substituted amino or adjacent X's may together form  $-C_4H_4(Y)_n$  - or



where Y is alkyl, alkoxy, hydroxy, aryl, substituted aryl, alkylthio, ether, thioether, amino or mono- or di-substituted amino and n has a value from 0-4,

25 each of R and R' is independently either a first bonding ligand incorporating a functional group which permits bonding to  $TiO_2$  or other semiconductor to be sensitized and which ligand can conduct an electron from an excited state of the phthalocyanine structure to the conduction band of  $TiO_2$  or other semiconductor when bonded thereto, or a second ligand which does not labilise the bond between

30 M and the first bonding ligand, providing at least one of R and R' is said first bonding ligand, and

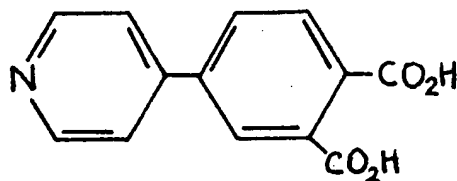
Q is nitrogen or -CZ- where Z is independently hydrogen, alkyl, alkoxy, hydroxy, aryl, substituted aryl, alkylthio, ether, thioether, amino or mono- or di-substituted amino,

5 providing that one at least of X, Y and Z is other than hydrogen.

Preferably, M is Ru.

Suitable first bonding ligands R or R' incorporate phosphonic acid, carboxylic acid,  
10 or possibly sulphonate groups. When R or R' incorporates an amine, it may be a straight or branched chain amine, or a cyclic or an aromatic amine such as pyridine, imidazole or triazole. The ligands may be mono- or poly-substituted with the afore-mentioned groups. Suitable ligands include 4-pyridine ethane-sulphonate, 3-pyridine sulphonate, pyridine-3-phosphonic acid, imidazole-4,5-dicarboxylic acid, 1,2,3-triazole-4,5-dicarboxylic acid,  
15 4-diphenylphosphinobenzoic acid, tris(4-carboxyphenylphosphine), 4-isocyanobenzoate, nicotinic acid, and especially preferred are pyridine-3,4-dicarboxylate and pyridine-4-phosphonic acid. Additionally, the TiO<sub>2</sub> bonding group may be separated from the metal binding site by a suitable linking group, eg

20



25 It is believed to be particularly desirable that ligand R or R', when bonded to TiO<sub>2</sub>, provides a  $\pi$  bonding system.

In the event that R or R' is a said second ligand, it may be CO or, preferably, a nitrogen donor such as an aliphatic, especially branched chain aliphatic, amine or a cyclic  
30 amine especially an aromatic amine. Such second ligands may carry substituents.

When X, Y or Z is alkyl or alkoxy, preferably each alkyl or alkoxy group has up to 8 carbon atoms, and may be branched chain.

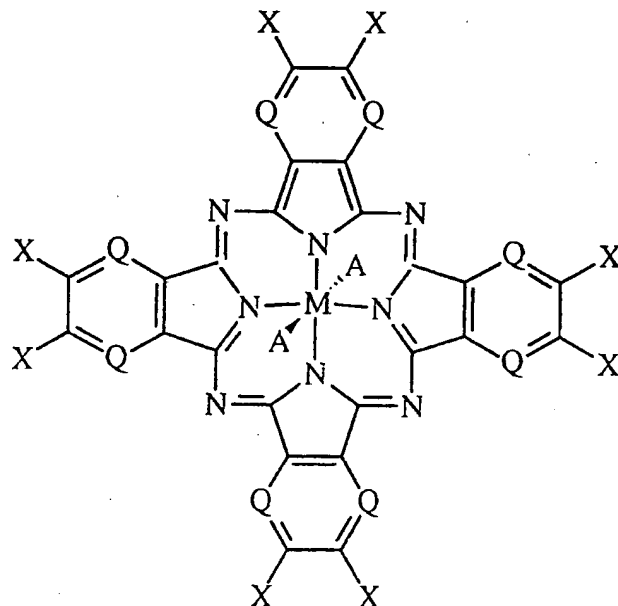
The compound may be in salt form, in which case the counterions are desirably  $K^+$ ,  
5  $Na^+$  or quaternary ammonium.

The compounds of formula I are novel, and may be prepared by a process comprising reacting a metal phthalocyanine compound of formula II,

10

15

20



II

wherein M, Q and X are as defined above, and A is an amine, preferably a pyridine group, CO (carbon monoxide) or a co-ordinating solvent, for example benzonitrile, with a salt of  
25 the ligand R, and isolating the product compound of formula I.

The reactants of formula II, and the salts of ligand R, are known from the literature or may be prepared by methods analogous to those known *per se*.

30 Suitably, the starting metal phthalocyanine or naphthalocyanine is mixed in an organic solvent, such as toluene, ethanol or 2-methoxy ethanol or a mixture of a water-

miscible organic solvent and water, such as an aqueous tetrahydrofuran, or immiscible solvent mixtures such as chloroform and water, with an excess, for example 2-10 fold stoichiometric, of the axial ligand, under an inert atmosphere, such as argon. The reaction is carried out desirably by heating, for example at reflux for about two days. The product  
5 may be isolated by the addition of a co-solvent to the reaction mixture. If required, the solubility of the product may be enhanced by exchanging the counterions, in generally known manner.

Where the axial ligands R in the compounds of the invention are not identical, it may  
10 be appropriate to prepare them by starting from a compound of formula II in which A is an amine suitable to act as the second ligand R. One of the ligands A may then be displaced with a salt of first ligand R in analogous manner to that described above. Alternatively, a compound of formula I in which both ligands R are identical aromatic amines may be prepared and one ligand R may be displaced using one equivalent of a non-aromatic amine.

15 It is believed that the present invention, by incorporating a bonding axial ligand, instead of the conventional substitution at the periphery of the Pc (see Sandoz WO 94/05025), has advantages and facilitates the synthesis of isomerically pure compounds. Experience with the RuN3 dye indicates that purity of the dye is both important and difficult  
20 to obtain. For optimum sensitizer efficiency, the redox potential of the ground and excited states need to be carefully optimised, as does the  $\lambda_{\max}$  of absorption. We believe that the present invention permits improved selection and "fine tuning" of properties for optimum photosensitization by substitution at the periphery of the phthalocyanine structure. Incorporation of a substrate-binding group at the periphery of the ring is thought to interfere  
25 with the optimisation of properties and hence design and preparation of the most efficient photosensitizers becomes even more difficult. The novel compounds have been found to be active in photosensitizing activity for TiO<sub>2</sub>-based photovoltaic devices as described hereafter. Moreover, some at least of the compounds possess a pleasing green colour, which increases the opportunity for commercial use of the compounds as photosensitizers.

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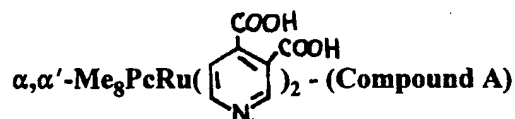
The novel compounds of the invention may be used in photovoltaic devices in generally known manner. The compounds show significantly improved performance over the previously specifically described phthalocyanines in the Sandoz WO 94/05025 and in our WO 93/09124, as will be shown hereafter.

5

Accordingly, the invention further provides a photovoltaic device based upon a film of  $\text{TiO}_2$ , wherein the  $\text{TiO}_2$  has deposited thereon a compound according to general formula I.

The invention will now be illustrated by the following Examples, which particularly describe aspects of the invention but in no way limit its scope.

#### EXAMPLE 1



15

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (43.37% Rh, 2.64g, 0.113mmol) was boiled in 1-pentanol (20ml) until a deep blue solution was obtained. This was added to a refluxing solution of 3,6-dimethylphthalonitrile (8.85g, 0.0566mol) and hydroquinone (0.62g, 0.0056mol) in 1-pentanol (60ml) under nitrogen. Ammonia gas was passed through the reaction flask and refluxing continued for 3 days. The cooled suspension was filtered, and the purple solid washed with pentanol (2x50ml) and then with methanol (3x25ml) and dried to give  $\alpha, \alpha'$ - $\text{Me}_8\text{PcRu}(\text{NH}_3)_2$  (4.81g) which was used without further purification.

20

$\alpha, \alpha'$ - $\text{Me}_8\text{PcRu}(\text{NH}_3)_2$  (4.81g) in benzonitrile (50ml) was refluxed under nitrogen for 24 hours. The purple solid was filtered off, washed into methanol (4x25ml) and dried to give  $\alpha, \alpha'$ - $\text{Me}_8\text{PcRu}(\text{PhCN})_2$  (3.80g).

25

Found: C 69.47%, H 4.58%, N 15.10%,  $\text{C}_{54}\text{H}_{42}\text{N}_{10}\text{Ru}$  requires C 69.6%, H 4.54%, N 15.0%.

30

$\alpha, \alpha'$ - $\text{Me}_8\text{PcRu}(\text{PhCN})_2$  (0.58g, 0.6mmol) and pyridine-3,4-dicarboxylic acid (0.45g, 2.7mmol) were refluxed under nitrogen and in the absence of light in 1:1 tetrahydrofuran



(THF)/water (190ml) for 80 hours. During this time additional THF was added as necessary to maintain the volume. The THF was then removed using a nitrogen stream and the product was collected by filtration. It was washed thoroughly with water and dried *in vacuo* to give purple crystals of  $\alpha,\alpha'$ -Me<sub>8</sub>PcRu(pyridine-3,4-dicarboxylic acid)<sub>2</sub>. Yield: 0.41g  
5 (IR C=O stretch 1734, 1708cm<sup>-1</sup>; HPLC analysis using reverse phase chromatography, 95% purity).

### EXAMPLE 2

10  $\alpha,\alpha'$ -(n-Octyl)<sub>8</sub>PcRu(pyridine-3,4-dicarboxylic acid)<sub>2</sub>

$\alpha,\alpha'$ -(n-Octyl)<sub>8</sub>PcRu(PhCN)<sub>2</sub> was reacted with excess pyridine-3,4-dicarboxylic acid in 1:1 THF/water. The mixture was heated to reflux overnight. The solvent was removed by evaporation and the residue was taken up in THF/petrol and filtered through silica. The  
15 silica was then extracted with THF and the product recovered as purple crystals by evaporation of the extract. (IR C=O stretch 1720 cm<sup>-1</sup>).

The compound  $\alpha,\alpha'$ -(n-decyl)<sub>8</sub>PcRu(pyridine-3,4-dicarboxylic acid)<sub>2</sub> is prepared in a similar manner.

20

### EXAMPLE 3

$\alpha,\alpha'$ -Me<sub>8</sub>PcRu(pyridine-3,5-dicarboxylic acid)<sub>2</sub>

25  $\alpha,\alpha'$ -Me<sub>8</sub>PcRu(PhCN)<sub>2</sub> (0.2g, 0.2mmol) and pyridine-3,5-dicarboxylic acid (0.14g, 0.8mmol) were refluxed under nitrogen and in the absence of light in 1:1 THF/water (190ml) for 80 hours. The THF was allowed to boil off to give a sticky blue/green residue in water. The solid was collected by filtration and then placed in a Soxhlet apparatus and the excess ligand was extracted with water overnight. The resulting solid was collected by filtration and  
30 washed with water (4×20ml) and then with diethyl ether (3×5ml) to give purple crystals of  $\alpha,\alpha'$ -Me<sub>8</sub>PcRu(pyridine-3,5-dicarboxylic acid)<sub>2</sub>. Yield: 0.21g. (IR C=O stretch 1724cm<sup>-1</sup>)

**EXAMPLE 4** **$\alpha,\alpha'$ -Me<sub>8</sub>PcRu(pyridine-4-hydroxamic acid)<sub>2</sub>**

5         $\alpha,\alpha'$ -Me<sub>8</sub>PcRu(PhCN)<sub>2</sub> (0.2g, 0.2mmol) and pyridine-4-hydroxamic acid (0.5g, 3.7mmol, 17eqs) were refluxed under nitrogen and in the absence of light in 1:1 ethanol/toluene (60ml) for 48 hours. The solvent was removed under reduced pressure and then the blue/green residue was stirred with water (20ml) for an hour to remove the excess ligand. The resulting solid was collected by filtration and washed with water (4×20ml) and  
10       then hexane (2×20ml) and dried to give  $\alpha,\alpha'$ -Me<sub>8</sub>PcRu(pyridine-4-hydroxamic acid)<sub>2</sub>. Yield: 0.19g. I.R. 1741, 1702, 1606 cm<sup>-1</sup>; HPLC analysis using reverse phase chromatography, 92% purity)

**EXAMPLE 5**

15

 **$\alpha,\alpha'$ -Me<sub>8</sub>PcRu(pyridine-3-phosphonic acid)<sub>2</sub>**

Pyridine-3-phosphonic acid (0.4g, 2.1mmol) and tetra-n-butylammonium hydroxide aqueous solution (3.7ml, 5.5mmol, 1.48M, 2eq) were refluxed in ethanol (25ml) for  
20       30 minutes. The solvent was removed under reduced pressure to give pyridine-3-tetra-n-butylammonium phosphonate.

$\alpha,\alpha'$ -Me<sub>8</sub>PcRu(PhCN)<sub>2</sub> (0.2g, 0.2mmol) and pyridine-3-tetra-n-butylammonium phosphonate (0.34g, 0.8mmol, in 3.1ml ethanol) were refluxed under nitrogen and in the  
25       absence of light in 1:1 ethanol/toluene (30ml) for 48 hours. The solvent was removed under reduced pressure and the blue/green residue was washed with 10ml 0.2M HCl. The solid was filtered off and washed with 0.2M HCl (10ml) and 80-100 petroleum ether (2×10ml) and dried to give  $\alpha,\alpha'$ -Me<sub>8</sub>PcRu(pyridine-3-phosphonic acid)<sub>2</sub>. Yield: 0.19g

30

**EXAMPLE 6** **$\alpha, \alpha'$ -Me<sub>8</sub>PcRu(pyridine-3-diethyl phosphonic ester)<sub>2</sub>**

5         $\alpha, \alpha'$ -Me<sub>8</sub>PcRu(PhCN)<sub>2</sub> (0.2g, 0.2mmol) and pyridine-3-diethyl phosphonic ester (0.2g, 0.8mmol in 16ml 1:1 toluene/ethanol) were refluxed under nitrogen and in the absence of light in 1:1 ethanol/toluene (40ml) for 60 hours. The solvent was removed under reduced pressure to give a blue/green residue. The solid was dissolved in chloroform (50ml) and shaken with 0.1M HCl (2×50ml) and then hexane (250ml) was added to the blue/green  
10 chloroform solution to precipitate a purple crystalline solid. The solid was filtered off and washed with hexane (2×20ml) and dried to give  $\alpha, \alpha'$ -Me<sub>8</sub>PcRu(pyridine-3-diethyl phosphonic ester)<sub>2</sub>. Yield 0.21g. IR. 1730 cm<sup>-1</sup>

**EXAMPLE 7**

15

 **$\alpha, \alpha'$ -(octyl)<sub>8</sub>PcRu(CO)(pyridine-3,4-dicarboxylic acid)**

$\alpha, \alpha'$ -(octyl)<sub>8</sub>PcH<sub>2</sub> (0.6g, 0.39mmol) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.32g, (0.5mmol) were refluxed together in benzonitrile (15ml) for 3 hours. Methanol was added and the mixture was  
20 filtered using silica gel. The gel was washed with methanol and the product was eluted using petroleum ether b.pt. 40-60°C/THF (4:1). This is a mixture of  $\alpha, \alpha'$ -(octyl)<sub>8</sub>PcRu(CO)(PhCN) and  $\alpha, \alpha'$ -(octyl)<sub>8</sub>PcRu(PhCN)<sub>2</sub>.

The eluent was evaporated and the solid redissolved in petroleum ether b.pt.  
25 40-60°C. The solution was heated to reflux and CO bubbled through until the reaction was complete as indicated by tlc (1 hour). The solution was then evaporated to dryness to give  $\alpha, \alpha'$ -(octyl)<sub>8</sub>PcRu(CO)(PhCN).

$\alpha, \alpha'$ -(octyl)<sub>8</sub>PcRu(CO)(PhCN) was heated to reflux with excess 3,4-pyridine-  
30 dicarboxylic acid, with small additions of aliquat and potassium carbonate, in 1:1 THF/water. After 3 days the solvent was evaporated and the mixture filtered through silica, eluting with

petroleum ether b.pt.40-60°C/THF. This eluted unreacted starting material. The silica was extracted with THF using a Soxhlet apparatus. The resulting solution was evaporated to yield the product  $\alpha,\alpha'$ -(octyl)<sub>8</sub>PcRu(CO)(pyridine-3,4-dicarboxylic acid).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  3.56 (s), 6.02(d) pyridine dicarboxylate ligand  
 $\delta$  4.65(m), 5.04 (m) PC-CH<sub>2</sub>-C<sub>7</sub>H<sub>15</sub>  
 (Other resonances for the pyridine dicarboxylate and the phthalocyanine ligand were not assigned due to the complexity of the spectrum).

Complexes PcRu(CO)(R) containing other phthalocyanines and R ligands may be obtained in an analogous manner.

Complexes containing a different ligand R' (e.g. where R' is a pyridine ligand different from R) may be obtained by displacement of the carbonyl ligand by photolysis in the presence of excess ligand R' according to known methods [D Dolphin, B R James, A J Murray and J R Thornback, Can J Chem (1980), 58, 1125].

The following compounds were prepared in an analogous manner to Example 1:

Compound		Found (required)		
		C	H	N
B	$\alpha,\alpha'$ -Me <sub>8</sub> PcRu(nicotinic acid) <sub>2</sub> 2MeOH	62.77 (62.60)	4.82 (4.86)	13.33 (13.52)
C	PcRu(pyridine-3,4-dicarboxylic acid) <sub>2</sub> 1.5H <sub>2</sub> O.EtOH	56.29 (56.47)	3.43 (3.46)	13.79 (13.72)
D	PcRu(pyridine-3,5-dicarboxylic acid) <sub>2</sub> 3H <sub>2</sub> O	55.10 (55.15)	3.27 (3.22)	13.91 (13.98)
E	NpRu(nicotinic acid) <sub>2</sub> .4H <sub>2</sub> O.2MeOH	58.64 (58.53)	3.80 (3.80)	11.03 (11.01)

Compound		Found (required)		
	$\beta,\beta'$ Me <sub>8</sub> PcRu(pyridine-3,4-dicarboxylic acid) <sub>2</sub> .CH <sub>3</sub> OH	60.52 (60.55)	4.02 (4.20)	12.46 (12.79)
	$\beta,\beta'$ (OMe) <sub>8</sub> PcRu(pyridine-3,4-dicarboxylic acid) <sub>2</sub>	54.04 (54.59)	3.65 (3.54)	11.54 (11.79)

5

The practical performance of the new compounds was tested as described below. An alcoholic solution of compound A was prepared. The absorption band in the visible has a maximum at 650nm ( $\epsilon 49'000 \text{ M}^{-1}\text{cm}^{-1}$ ) and that of the phosphorescence is located at 895nm the triplet state lifetime being 474ns under anaerobic conditions. The emission is entirely quenched when compound A is adsorbed onto a nanocrystalline TiO<sub>2</sub> film. The compound was deposited by dipping a mesoscopic anatase film (thickness *ca* 10 $\mu$ , coated onto conducting glass, LOF TEC 10, fluorine-doped SnO<sub>2</sub> sheet resistance 10 ohm/square) as previously described in J Am Chem Soc, 1993, 115, 6382) for several hours in a 3x10<sup>-4</sup> M solution in ethanol containing 50mM 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid (Cheno) and 2.5% DMSO. The presence of Cheno is necessary to avoid surface aggregation of the sensitizer. The visible band in the absorption spectrum of compound A is red shifted by 10nm upon adsorption.

Very efficient quenching of the emission of compound A was found to be due to electron injection from the excited triplet state of phthalocyanine into the conduction band of the TiO<sub>2</sub>. The photocurrent action spectrum is shown in Figure 1 where the incident photon to current conversion efficiency (IPCE) is plotted as a function of wavelength. The feature is extending well into the near IR region displaying a maximum around 660nm where the IPCE exceeds 50%. It may be that the pyridyl orbitals do not participate in the  $\pi,\pi^*$ -excitation which is responsible for the 650nm absorption band of compound A, but electronic coupling of its excited state to the Ti (3d) conduction band manifold is strong enough through this mode of attachment to render charge injection very efficient.

The occurrence of electron transfer was further confirmed by time resolved nanosecond Nd-YAG laser experiments shown in the inset of Figure 1. The end of pulse transient spectrum indicates bleaching of the ground state absorption of compound A and the appearance of new features in the wavelength range of 700 to 800nm and the 480 to 580nm. These bands are attributed to the formation of the cation radical of the phthalocyanine. The recovery of the ground state spectrum due to charge recombination occurs on a time scale of several hundred microseconds indicating that re-capture of the conduction band electron by the oxidised dye is a relatively slow process.

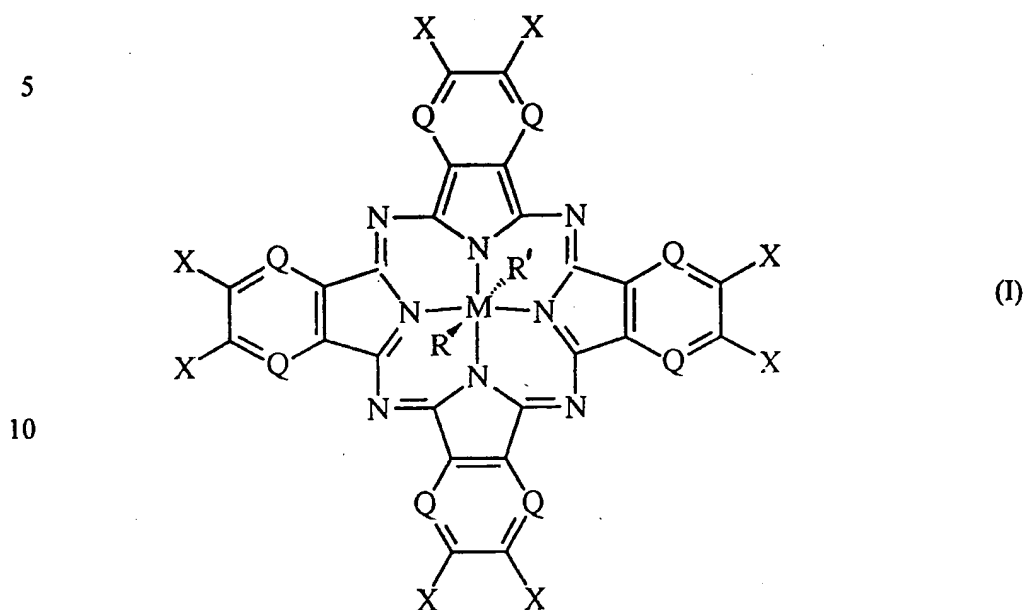
Our results establish a new pathway for grafting phthalocyanines to oxide surfaces through axially attached ligands. Using such a film in a sandwich type cell configuration as described in the J Am Chem Soc paper in conjunction with a 1 M LiI/0.05 M LiI<sub>3</sub> redox electrolyte, photocurrents over to 10 mA/cm<sup>2</sup> were readily obtained under simulated AM 1.5 solar radiation. These are by far the highest conversion efficiencies ever observed with phthalocyanine-type sensitisers.

Standard literature tests were performed on compound A and compounds B to E identified above, and are tabulated below.

Compound	$\tau f$ (ns)	$E_{o-o}$ (eV)	$E_{1/2}$ V vs SCE	Current mA/cm <sup>2</sup> at 1 Sun PC/LII/I <sub>2</sub>	Uoc(mV) at 1 Sun PCLiI/I <sub>2</sub>
A	344	1.410	0.6	11.0	500
B	221	1.352		2.9	531
C	336	1.403	0.76	5.7	417
D	348	1.405		4.6	465
E		1.258		2.1	460

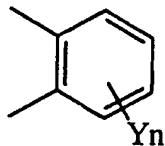
**CLAIMS**

1. Transition metal phthalocyanine-type derivatives of formula I,



wherein M is Ru, Rh, Os, Ir or Pt

- 15 each X is hydrogen, alkyl, alkoxy, hydroxy, aryl, substituted aryl, alkylthio, ether, thioether, amino or mono- or di-substituted amino or adjacent X's may together form  $-C_4H_4(Y)_n$  - or



20

where Y is alkyl, alkoxy, hydroxy, aryl, substituted aryl, alkylthio, ether, thioether, amino or mono- or di-substituted amino and n has a value from 0-4,

R and R' are independently either a first bonding ligand incorporating a functional group which permits bonding to TiO<sub>2</sub> or other semiconductor to be sensitized and which ligand can conduct an electron from an excited state of the phthalocyanine structure to the conduction band of TiO<sub>2</sub> or other semiconductor when bonded thereto, or a second ligand which does not labilise the bond between M and the first bonding ligand, providing at least one of R and R' is said first bonding ligand, and

Q is nitrogen or -CZ- where Z is independently hydrogen, alkyl, alkoxy, hydroxy, aryl, substituted aryl, alkylthio, ether, thioether, amino or mono- or di-substituted amino, providing that one at least of X, Y and Z is other than hydrogen.

2. Derivatives according to claim 1, wherein M is Ru.

3. Derivatives according to claim 1 or 2, wherein when R or R' is a bonding ligand, it incorporates one or more phosphonic acid, carboxylic acid or sulphonate functional groups.

4. Derivatives according to any one of claims 1 to 3, wherein R or R' incorporates a straight or branched chain amine or a cyclic or aromatic amine.

5. Derivatives according to any of claims 1 to 4, wherein R or R' is selected from 4-pyridine ethane sulfonate, 3-pyridine sulfonate, pyridine-3-phosphonic acid, imidazole-4,5-dicarboxylic acid, 1,2,3-triazole-4,5-dicarboxylic acid, 4-diphenylphosphinobenzoic



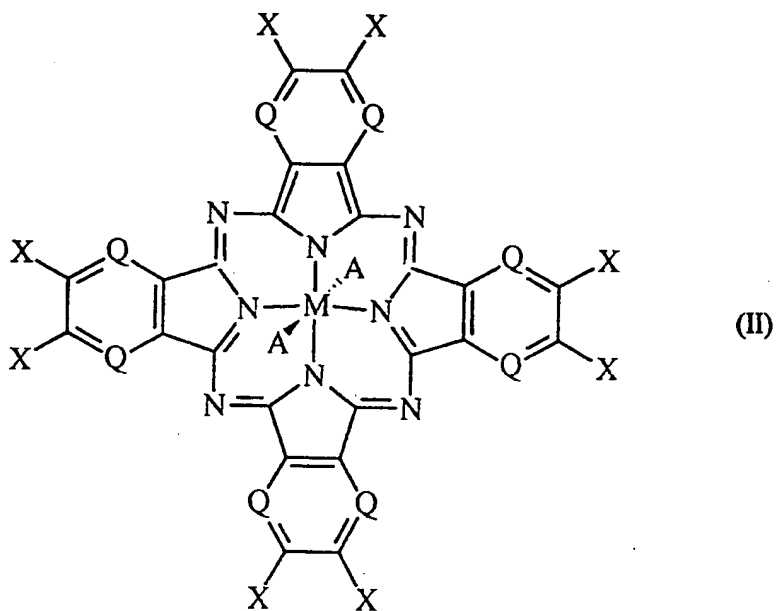
acid, tris(4-carboxyphenylphosphine), 4-isocyanobenzoate, nicotinic acid, pyridine-3,4-dicarboxylate and pyridine-4-phosphoric acid.

6. Derivatives according to any of claims 1 to 5, wherein one of R and R' is CO.

5

7. Derivatives according to any one of claims 1 to 5, wherein one or more of X, Y or Z is alkyl or alkoxy of up to 8 carbon atoms, in which the alkyl groups are straight or branched chains.

10 8. A process for the production of a derivative according to claim 1, in which R=R' comprising reacting a metal phthalocyanine compound of formula II,



wherein M, Q and X are as defined in claim 1, and A is an amine, with a salt of the ligand R as defined in claim 1, and isolating the product derivative of formula I.

9. A process according to claim 8, carried out in an organic solvent, a mixture of a  
5 water-miscible organic solvent and water or a mixture of an immiscible organic solvent and water in the presence of a stoichiometric excess of the salt of the ligand R, under an inert atmosphere.

10. A process for the production of a derivative of formula I as defined in claim 1 and  
10 in which R is not the same as R', comprising the reaction of the corresponding non-metallated phthalocyanine with  $\text{Ru}_3(\text{CO})_{12}$  and a bonding ligand, to form the derivative of formula I in which R or R' is CO and the other of R and R' is the bonding ligand, and where desired, displacing the carbonyl ligand with another ligand.

15 11. The use of derivatives according to any of claims 1 to 7 as sensitizers for semiconductors in a dye solar cell.

12. The use of a derivative according to any of claims 1 to 7 in combination with  $\text{RuN}_3$   
as a sensitizer for semiconductors in a dye solar cell.

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13. An optically transparent device incorporating a dye solar cell in which the dye comprises a derivative according to any of claims 1 to 7.

14. A dye solar cell in which the dye comprises a derivative according to any of claims 1 to 7.

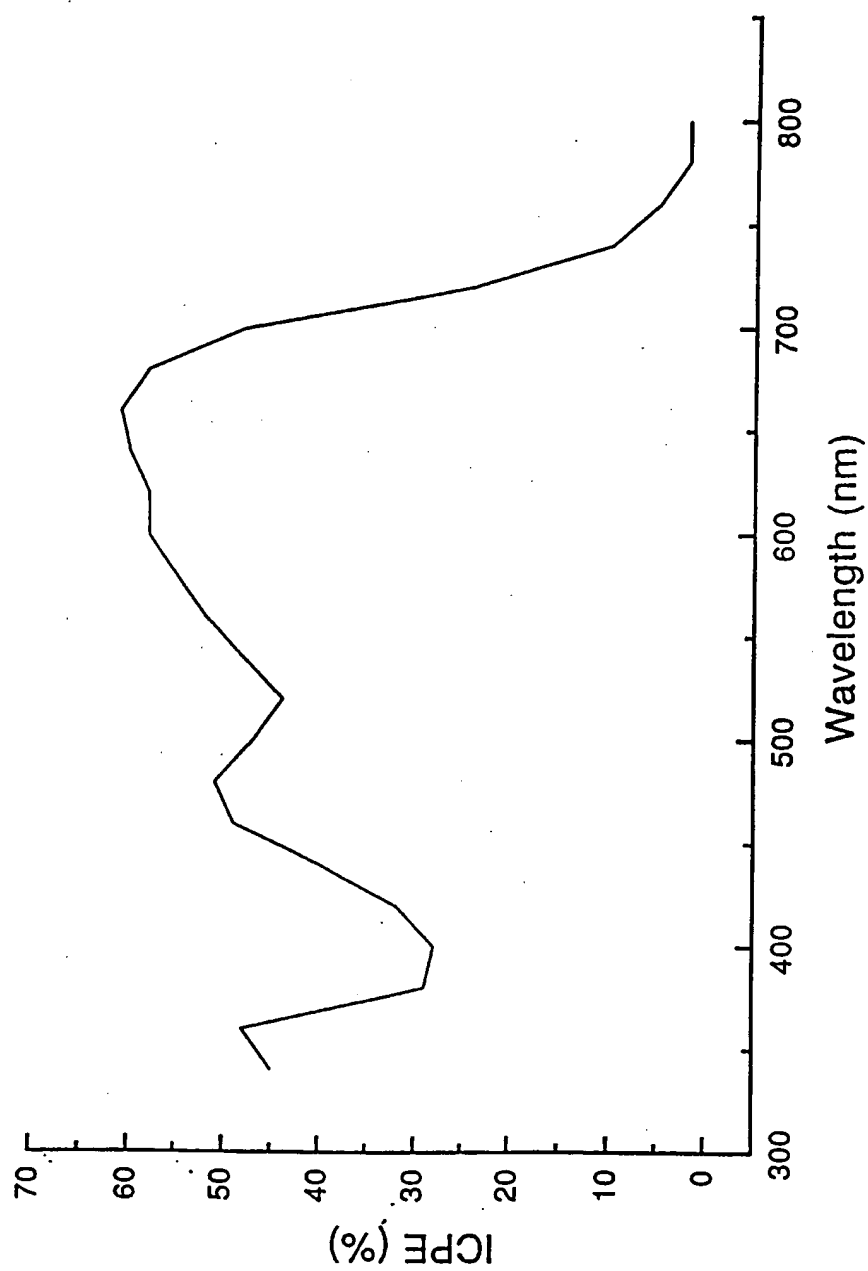
15. A window for a building comprising a dye solar cell according to claim 14.

5

16. A method of generating electricity from sunlight comprising the use as a sensitizer for a semiconductor in a dye solar cell, of a derivative according to any of claims 1 to 7.

1/1

Figure 1: Compound of Example A, incident photon to current conversion efficiency



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01872

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C07F15/00 H01G9/20

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 09124 A (JOHNSON MATTHEY PLC) 13 May 1993 cited in the application see the whole document --- -/--	1-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

27 August 1998

Date of mailing of the international search report

09/09/1998

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01872

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 126, no. 19, 12 May 1997 Columbus, Ohio, US; abstract no. 248333, VOLLANO, J. F. ET AL: "The synthesis and in vitro photodynamic activity of a series of novel ruthenium(II)-2,3-naphthalocyanines" XP002075710 see abstract & J. PHOTOCHEM. PHOTOBIOLOG., 8 (1997), 37(3), 230-235 CODEN: JPPBEG; ISSN: 1011-1344, 1997, ----	1-10
A	WO 91 16719 A (GRAETZEL, M. ET AL.) 31 October 1991 cited in the application see the whole document ----	1-16
P, X	NAZEERUDDIN, MD. K. ET AL: "Efficient near IR sensitization of nanocrystalline TiO2 films by ruthenium phthalocyanines" CHEM. COMMUN. (CAMBRIDGE) (1998), (6), 719-720 CODEN: CHCOFS; ISSN: 1359-7345, 1998, XP002075709 see the whole document -----	1-16

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In International Application No

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